

Incoherent tunneling surface diffusion for interacting adsorbates

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The incoherent tunneling surface diffusion of light atoms is analyzed in terms of a Chudley-Elliott master equation constrained to nearest neighbors for moderate to high temperatures (above the crossover surface temperature). Recent helium spin-echo measurements for diffusing H and D atoms on a Pt(111) surface are thus examined within the framework of the so-called bounce technique. A good agreement is found between theory and experiment, with the substrate friction coefficients obtained being of the order of those reported in the literature for this kind of systems. Furthermore, following this model, an increase of the tunneling rate is predicted for decreasing surface coverages.

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Hydrogen diffusion on metal surfaces has been the subject of an intensive applied and fundamental research for many years [1–6]. The involvement of this process in the design of fuel cells or in the storage of H₂ makes it of technological interest. Therefore, at a fundamental level, a good understanding of this dynamics is essential, for it provides important information on the adiabatic interaction between adsorbate and substrate. Indeed, because atomic hydrogen is the simplest element that may undergo chemisorption, its motion on a weakly corrugated surface constitutes a benchmark to study two possible competing diffusion processes: classical (activated) *over-barrier* hopping *versus* quantum-mechanical *under-barrier* tunneling. In the classical regime, the rate decreases with temperature until reaching the tunneling regime, where the corresponding rate approaches a constant, temperature-independent value. It is worth stressing that, apart from diffusion problems (in the bulk or on surfaces), this typical behavior can also be found in many chemical reactions or processes [7–9].

According to recent He spin-echo (HeSE) measurements of H and D diffusion on Pt(111) [6] at a low coverage ($\theta = 0.1$ ML) and their ulterior analysis, there is a significant contribution of quantum effects for temperatures ranging from 80 K to 250 K, well above the (assumed) crossover temperature to deep tunneling, $T_c \approx 65$ K. As it is shown, quantum motion takes place mainly through incoherent tunneling between nearest-neighbor sites, which furnishes strong support for a dissipative transition-state theory (TST) description. The analysis of surface diffusion processes by means of this theory allows [8] to determine hopping rates, diffusion constants, friction coefficients, etc. Therefore, the mobility of adparticles along the surface as a function of the temperature and/or the coverage can be closely described. In the particular case of Ref. 6, the authors consider that the expression for the hopping rate is given by [10]

$$\Gamma = \frac{3\omega_0}{2\pi} \Xi x_b \exp(-E_a/k_B T), \quad (1)$$

where ω_0 is the vibration frequency at the adsorption site, the factor 3 reflects the number of possible jump directions, E_a is the barrier activation energy, k_B is Boltzmann's constant, and T is the surface temperature. In the Ohmic regime, the expression $2x_b\omega_b = -\gamma + \sqrt{4\omega_b^2 + \gamma^2}$ gives the friction-dependent barrier frequency, where γ is the friction, x_b is the dimensionless Kramers' factor, and ω_b gives the vibration frequency of the inverted potential at the transition state. On the other hand, Ξ accounts for the quantum, temperature-dependent correction prefactor [8, 10],

$$\Xi = \prod_{n=1}^{\infty} \frac{\omega_0^2 + \nu_n^2 + \nu_n \gamma}{-\omega_b^2 + \nu_n^2 + \nu_n \gamma}, \quad (2)$$

where $\nu_n = 2\pi n/\hbar\beta$ are the so-called Matsubara frequencies. When applied to the experimental data [6], this model renders $\omega_0 = 31$ meV for H, $\omega_b/\omega_0 = 5.4$ and $E_a = 83$ meV for both H and D diffusion, $x_b = 0.21$ for H, and $x_b = 0.29$ for D. Because both ω_b and ω_0 scale as $m^{-1/2}$, the values corresponding to D can be readily obtained by considering the multiplying factor, $\sqrt{m_H/m_D}$. With these parameters, the crossover temperature $T_c = \hbar\omega_b x_b / 2\pi k_B$ [8] gives $T_c \approx 65$ K for H and $T_c \approx 63$ K for D, which indicates that the range of temperatures in the experiment is above the crossover temperature. According to this model, the conclusion arising from the fittings reported in [6] is that the hopping for both H and D is dominated by tunneling, with the corresponding rates displaying a certain curvature in the region of lower temperatures. However, when the friction coefficient γ is evaluated for each adparticle, it is found that $\gamma_H \approx 1.15$ ns⁻¹ and $\gamma_D \approx 0.57$ ns⁻¹, which display the correct factor 2 between them, but are unexpectedly large compared to systems involving heavier particles [11].

Here we analyze these experimental findings by means of an alternative approach based on the so-called bounce technique, which allows to determine rates whenever the range of parameters (surface temperature and friction)

are such that the diffusing adparticle tunnels coherently and incoherently [9, 12, 13]. In particular, in the incoherent tunneling regime, a master equation scheme, the so-called Chudley-Elliott model from surface diffusion [14, 15], rules the corresponding dynamics. When considering the dynamics on a surface, adparticles are moving in a two-dimensional periodic lattice of binding sites. In the case of activated diffusion, where the thermal energy is higher than the barrier height, adparticles are mainly assumed to perform discrete jumps between neighboring sites. Within the Chudley-Elliott model, this jump diffusion dynamics on a two-dimensional Bravais lattice is accounted for by a master equation in terms of the van Hove $G(\mathbf{R}, t)$ -function (or time-dependent pair correlation function) [16], widely used to describe a statistical ensemble of interacting particles. Thus, given a particle at the origin at some arbitrary initial time $t = 0$, $G(\mathbf{R}, t)$ gives the averaged probability of finding the same or another particle at the surface position \mathbf{R} at time t . Notice that this function generalizes the well-known pair distribution function $g(\mathbf{R})$ from statistical mechanics [17] by providing information about the interacting particle dynamics. The master equation corresponding to incoherent tunneling can be expressed in general as

$$\dot{G}(\mathbf{R}, t) = \sum_{\mathbf{j}} \nu_{\mathbf{j}} G(\mathbf{R} + \mathbf{j}, t), \quad (3)$$

where $\nu_{\mathbf{j}}$ accounts for the tunneling rate involved in the transition between the lattice point \mathbf{R} and the nearby one $\mathbf{R} + \mathbf{j}$, with \mathbf{j} being the jump vector among different lattice points running over all lattice vectors (positive, negative, and even zero). In the case of light particles, such as H and D, and for thermal energies lower than the barrier height, a tunneling-mediated diffusion process is expected to dominate this nearest neighbors dynamics [6].

The space Fourier transform of the G -function is the intermediate scattering function, which reads as

$$I(\Delta\mathbf{K}, t) = \langle e^{-i\Delta\mathbf{K} \cdot \mathbf{R}(t)} e^{i\Delta\mathbf{K} \cdot \mathbf{R}(0)} \rangle, \quad (4)$$

with the brackets denoting an ensemble average. This function measures the time correlation loss for a given parallel (along the surface) momentum transfer of the probe particle, $\Delta\mathbf{K}$. Therefore, it can also provide us with information about friction coefficients at different coverages and (surface) temperatures along with the observed $\Delta\mathbf{K}$ direction. Without loss of generality, along this direction the diffusion process can be assumed to be one-dimensional among the different wells formed by the surface corrugation, so that the intermediate scattering function can then be expressed as a Fourier series as

$$I(\Delta K_{\parallel}, t) = \sum_n G_n(t) e^{i\Delta K_{\parallel} n}, \quad (5)$$

where ΔK_{\parallel} is a dimensionless momentum transfer resulting from the projection of the lattice vector \mathbf{j} along

the direction pointed by $\Delta\mathbf{K}$ multiplied by the lattice constant a , i.e., $\Delta K_{\parallel} = a\|\Delta\mathbf{K}\| \cos \alpha$, with α being the angle between $\Delta\mathbf{K}$ and \mathbf{j} . Here, only first neighbors are considered and therefore, given the geometry of the two-dimensional lattice for the Pt(111) surface [1], for four of these neighbors $|\Delta K_{\parallel}| = a\Delta K \cos(\pi/6)$, while for the other two $\Delta K_{\parallel} = 0$. Regarding n , it labels the n -th well of the binding site (bearing in mind this tight-binding like model). Now, for nearest neighbors, Eq. (3) can be expressed in terms of the $G_n(t)$ coefficients as

$$\dot{G}_n(t) = \nu_{n-1}^+ G_{n-1}(t) + \nu_{n+1}^- G_{n+1}(t) - (\nu_n^+ + \nu_n^-) G_n(t), \quad (6)$$

which is precisely the same expression provided by Weiss and Grabert for incoherent tunneling in a periodic potential [13]. Within this context, the rates $\nu_{n\mp 1}^{\pm}$ in the above expression give the tunneling rate from the $(n\mp 1)$ -th well to the n -th one, while \pm account for the tunneling rates to the right or left neighboring well, respectively. Tunneling rates are assumed to be equal for the left or right direction and independent of the well site. The differential equation (6) can be solved analytically for the initial conditions, $G_n(0) = \delta_{n,0}$. From it, the intermediate scattering function is written as

$$\begin{aligned} I(\Delta K_{\parallel}, t) &= e^{-2\bar{\Gamma}t \sin^2(\Delta K_{\parallel}/2)} = e^{-\bar{\Gamma}t} e^{\bar{\Gamma}t \cos(\Delta K_{\parallel})} \\ &= e^{-\bar{\Gamma}t} \sum_{n=-\infty}^{\infty} I_n(\bar{\Gamma}t) e^{i\Delta K_{\parallel} n}, \end{aligned} \quad (7)$$

where I_n is the modified Bessel function of integer order n and $\bar{\Gamma} = \nu/2$ describes the global tunneling rate. Equation (7) is precisely the function recorded in the HeSE technique [6].

The bounce technique [9, 12, 13] enables an analytical expression for $\bar{\Gamma}$, which reads as

$$\bar{\Gamma} = \frac{\sqrt{\pi}}{2} \frac{\Delta^2}{\omega_0} \left(\frac{\pi k_B T}{\hbar \omega_0} \right)^{2\zeta-1} \frac{\Gamma(\zeta)}{\Gamma(\zeta + 1/2)}. \quad (8)$$

In this expression, $\Gamma(\cdot)$ denotes the Gamma function, Δ is the dressed tunnel matrix expressed as a function of the so-called bare tunnel matrix Δ_0 [9], and ζ represents a dimensionless friction coefficient, given by

$$\zeta = \frac{ma^2}{2\pi\hbar} \gamma. \quad (9)$$

Within this analytical model, the diffusion coefficient can also be obtained through the relation $D = a^2 \bar{\Gamma}$ where one clearly sees that the usual Einstein relation does not hold, since it does not scale with the friction coefficient as γ^{-1} .

Experimentally, the tunneling (or hopping) rates $\bar{\Gamma}$ are obtained after carrying out a best-fit procedure through Eq. (8) for a given momentum transfer, temperature and coverage. In Fig. 1, it is displayed the fitting of the experimental tunneling rates for H (experiment: blue open circles; fitted values: blue solid line) and D (experiment:

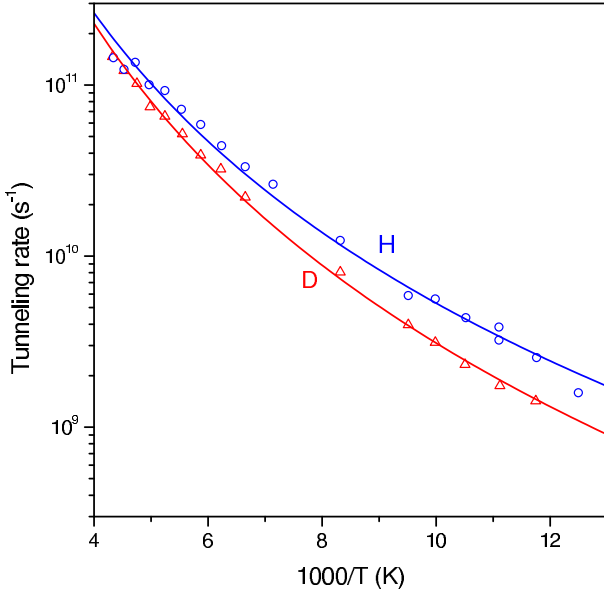


FIG. 1: Tunneling rates as a function of temperature for H (experiment: blue open circles; fitted values: blue solid line) and D (experiment: red open triangles; fitted values: red solid line) for a coverage $\theta = 0.1$ ML.

red open triangles; fitted values: red solid line). In both cases, the coverage is $\theta = 0.1$ ML and temperatures range from 80 K to 250 K. Although the quality of the fitting is as good as in Ref. [6], here only two parameters were needed: a multiplying prefactor, C , and the friction coefficient η [through Eq. (9)], i.e.,

$$\bar{\Gamma}_{\text{fit}} = C \left(\frac{1000}{T} \right)^{1-2\zeta}. \quad (10)$$

After substituting the corresponding values into Eq. (9), we find that the friction coefficients are $\gamma = 13.6 \text{ ps}^{-1}$ for H and $\gamma = 7.4 \text{ ps}^{-1}$ for D, which are much smaller than those previously reported [6] and closer to those for heavier adsorbed species [11]. The prefactors obtained are $C = \exp(32.21)$ for H and $C = \exp(32.66)$ for D. From Eq. (9), we also find that the friction coefficient for D is roughly a factor 2 smaller than for H, in agreement with the mass scaling factor expected for this coefficient, m^{-1} (isotopic effect). Finally, due to the fact $\zeta > 1$ for both H and D ($\zeta_{\text{H}} = 2.63$ and $\zeta_{\text{D}} = 2.85$) we would like to stress the suitability and validity of this model to describe the range of temperatures considered here; even valid down to zero surface temperature as stated by Grabert and Weiss [12].

In order to analyze the dependence on the surface coverage, an alternative fitting has also been considered by using a temperature-dependent collisional-friction model, the so-called two-bath model [18–20]. Within this new model, one bath describes the effect of surface phonons, while the other one accounts for the collisions among the interacting adsorbates. These baths are assumed to

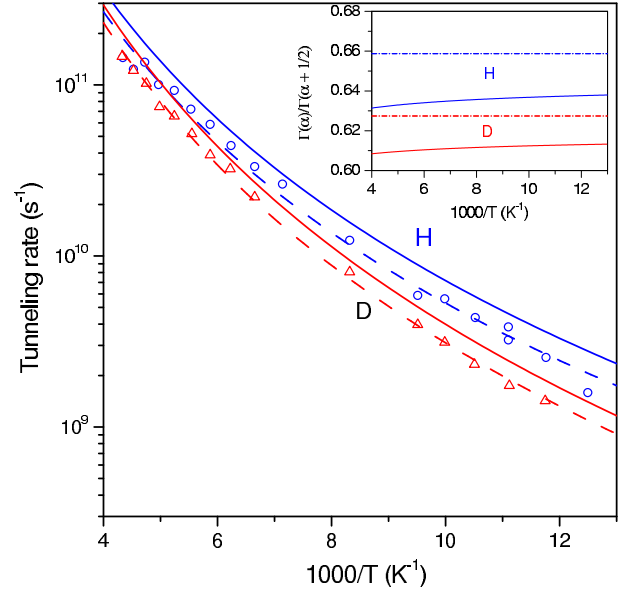


FIG. 2: Tunneling rates as a function of temperature for H (blue solid line) and D (red solid line) for a coverage of $\theta = 0.01$ ML. For comparison, the same curves from Fig. 1 are plotted for a coverage of $\theta = 0.1$ ML but fitted to the so-called two-bath model (see text). In the inset, the negligible variation of the prefactor $\Gamma(\zeta)/\Gamma(\zeta + 1/2)$ along the range of temperatures studied is also shown (solid lines: $\theta = 0.1$ ML; dashed-dotted line: $\theta \approx 0$ ML).

be uncorrelated and therefore the corresponding frictions are additive. Accordingly, the total friction, η , is now a sum of two contributions: the usual substrate friction, γ , and a collisional friction, λ , accounting for the collision among adsorbates ($\eta = \gamma + \lambda$). For a simple estimation of the dependence of λ on the coverage, one can consider [19] the elementary kinetic theory of transport in gases [17] as well as the Chapman-Enskog theory for hard spheres. This procedure renders a simple relationship between the collisional friction λ and the coverage θ at a certain temperature T ,

$$\lambda = \frac{6\rho\theta}{a^2} \sqrt{\frac{k_B T}{m}}, \quad (11)$$

where ρ is the effective radius of the adparticle. Thus, by increasing the coverage, the collisional friction is also increased and therefore the total friction. This allows us to extend straightforwardly our expressions for quantum diffusion by tunneling to different coverages (up to more or less 15% for this model). In order to distinguish in the friction coefficient the contributions coming from the surface and from the collisions, the fitting was carried out expressing the exponent in (8) as $1 - b\gamma - c\sqrt{T/1000}$.

Following the fitting procedure mentioned above with the available experimental data, the curves for $\theta = 0.1$ ML have again been computed, finding $C = \exp(32.54)$, $b = 0.388 \text{ ps}$, $\gamma = 13.56 \text{ ps}^{-1}$, and $c =$

0.462 K^{-1/2} for H, and $C = \exp(32.93)$, $b = 0.775$ ps, $\gamma = 7.34$ ps⁻¹, and $c = 0.382$ K^{-1/2} for D. The newly fitted curves for $\theta = 0.1$ ML, displayed in Fig. 2 (blue and red dashed lines for H and D, respectively), again show a fairly good agreement with both the experiment and the fitting curves displayed before (see Fig. 1). Furthermore, the values of the substrate friction γ are similar with those found before assuming that all friction effects were included in η fulfilling the isotopic effect. Now, according to this new functional dependence of the tunneling rate on the coverage and surface temperature, if we consider $c = c'\theta/0.1$, then the curves for a lower coverage can also be readily determined, e.g., for $\theta = 0.01$ ML, as seen in Fig. 2 (blue and red solid lines for H and D, respectively). Moreover, this fitting model also allows us to justify our former preassumption that the multiplying factor $\Gamma(\zeta)/\Gamma(\zeta+1/2)$ can be considered to be a constant. As seen in the inset of Fig. 2, the variation of this function along the range of temperatures considered when ζ is expressed as a function of temperature increases only about 1% for H and 0.8% for D as T decreases in the case of $\theta = 0.1$ ML (for $\theta \approx 0$ this increment is meaningless). This prediction thus shows that a decrease in the total friction (e.g., by lowering the coverage or equivalently the collisional friction) leads to an enhancement of tunneling which is consistent with our model. This behavior is no longer valid for higher coverages (greater than 15 %) as reported by previous experimental results of the same systems by using the helium atom scattering technique and analyzed in terms of an Arrhenius law [1]. Therefore, the application of this two-bath model could be extended to higher coverages letting λ free for the fitting procedure.

To conclude, the characteristic temperature power law (8) proposed by Grabert and Weiss [12, 13] for tunneling rates is apparently valid at all temperatures (even zero temperature) provided $\zeta > 1$, as it is in our case. Indeed, the application of the Chudley-Elliott master equation to describe the incoherent tunneling together with the use of such a rate have rendered values for the friction parameters in the order of the ps⁻¹, which are within the expected range. In general, the loss mechanism may come from the lattice relaxation and/or the electronic contribution. As reported by Sundell and Wahnström [3], this typical power law was first suggested by Kondo [21] and seems to be related to the electronic contribution, i.e., the non-adiabatic response of the conduction electrons to the adparticle (H or D) motion. Nevertheless, in view of the temperature-dependent behavior discussed elsewhere [12, 13] and also presented here, the use of this power law seems to be more general, and valid for any loss mechanism or a sum of several uncorrelated loss mechanisms (sum of friction coefficients due to electrons, phonons, and adsorbates). If the fitting of the experimental results is quite good in a very wide range of sur-

face temperatures, where over-barrier hopping should be predominant for heavier adsorbates, one may conclude that quantum effects are relevant in the diffusion of light adparticles. Apparently, the TST framework does not follow such a power law leading to a limited application at low surface temperatures.

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